

PATENT SPECIFICATION

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(54) UNSATURATED POLYESTERS, THEIR PRODUCTION AND USE

(71) We, SCOTT BADER COMPANY LIMITED, of Wollaston, Wellingborough, Northamptonshire, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel unsaturated polyesters, and to their production and use.

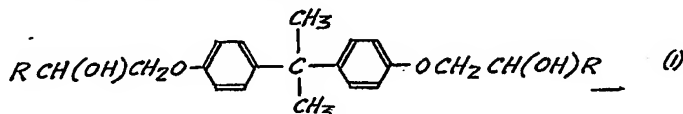
Unsaturated polyesters resins have been known for many years and they are conventionally prepared by the condensation, at temperatures around 200°C, of one or more unsaturated dicarboxylic acids or anhydrides, optionally with one or more saturated dicarboxylic acids or anhydrides, with one or more glycols. For specific purposes one or more monocarboxylic acids, polycarboxylic acids, monohydric alcohols or polyhydric alcohols can be included in minor amounts. The condensation reaction is commonly continued until an acid value in the range 5—50 mg KOH/g is reached, after which the product is cooled and blended with a monomer containing one or more vinyl groups ($>C=CH_2$). At this stage an inhibitor is added to prevent premature gelation.

These liquid mixtures can be cured or converted to the solid form by the action of free radical catalysts and heat or by the action of free radical catalysts and promoters (the so-called accelerators) at room temperatures or below.

A description of the properties and uses of some commercially available polyester resins can be found in our 'Polyester Handbook' (1969 Edition).

The properties of the polyester resins in the cured state can be varied widely by the choice of raw materials used.

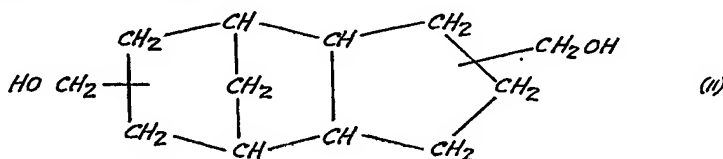
For example it is generally acknowledged that resins containing glycols which are based on Bisphenol A and which are of the formula



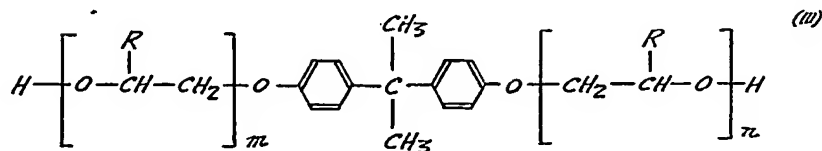
where R is a hydrogen atom or a methyl group, show good chemical resistance.

However, such polyesters are brittle and have low elongations at break (about 1.5%) which limits their usefulness in laminated structures. Attempts have been made to reduce the brittleness, but the chemical resistance is reduced and the heat deflection temperatures of the cast resins are lowered. According to the present invention we provide an unsaturated polyester which comprises the residues of

(a) a glycol of the formula



and (b) a glycol of the formula



where R represents a hydrogen atom or a methyl group, and m and n are numbers and each has an average value of at least 1.5, preferably 2 or more; and (c) at least one ethylenically unsaturated dicarboxylic acid.

We also provide a resin composition comprising an unsaturated polyester as defined in the preceding paragraph and a copolymerisable monomeric ethylenically unsaturated compound. We have discovered that such a composition, on curing, possesses good chemical resistance together with improved elongation properties.

The unsaturated polyester of the invention thus comprises the esterification product of an acid component including an unsaturated organic dicarboxylic acid and of a hydroxy component comprising a mixture of dihydric alcohols including as essential components a compound of formula (II) and a compound of formula (III).

Mixtures of two or more glycols of formula (II) can be used. A particularly preferred material is that sold under the trade name TCD-Alcohol DM by Farbwerke Hoechst AG (vormals Meister Lucius & Brüning), which is a mixture of alcohols, consisting of isomeric, tricyclic, primary C_{12} diols, prepared by oxo-synthesis from purified dicyclopentadiene (according to the manufacturers' published literature).

The preferred glycols of formula (III) are those in which m and n are at least 2 and not more than about 6. Particularly preferred glycols of formula (III) are those obtained by reacting 4 moles of ethylene oxide or of propylene oxide with 1 mole of Bisphenol A.

The glycols of formulae (II) and (III) are essential ingredients of the polyester; however other dihydroxy compounds may be incorporated into the reaction mixture in minor proportions, for example ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, 1,4-butane diol and 1,6-hexane diol. Such dihydroxy compounds may comprise, for example, up to 5 molar percent of the total hydroxy component. If desired minor proportions of a monohydric alcohol may also be added, such as butanol.

Especially preferred polyesters are prepared using a mixture of a glycol (or glycols) of formula (II) with a glycol of formula (III), preferably in a molar ratio between 1:2 and 2:1 and especially 1:1.

The preferred ethylenically unsaturated acids are maleic acid and fumaric acid. In addition to the ethylenically unsaturated acids, the reaction mixture for preparing the polyesters, of the invention may also incorporate (in proportions of, for example, up to 10 molar percent of the acid component of said polyester) saturated and/or aromatic acids, such as phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, sebacic acid, and adipic acid. The corresponding anhydrides can also be used and are often preferred in place of those acids which form anhydrides, e.g. maleic anhydride, itaconic anhydride and phthalic anhydride. The term "dicarboxylic acid" as used herein includes such anhydrides. Minor proportions (for example, up to 5 molar percent of said acid component) of higher polycarboxylic acids, such as 1,2,3-benzenetricarboxylic acid or trimellitic anhydride, or of monocarboxylic acids, such as stearic acid, may also be incorporated in the polyester.

The polyesters of the invention may be prepared by conventional techniques, for example by polyesterification of the acid or acids with the mixture of dihydroxyl materials (and any other ingredients) at a temperature of 190° to 200°C , preferably in an inert atmosphere, the reaction being carried on until an acid value less than 25 mg KOH/g is obtained. In a preferred process a slow stream of oxygen-free nitrogen is bubbled through the reaction mixture. The resulting polyester can then be blended with the ethylenically unsaturated copolymerisable monomer to form the resin composition of the invention. As monomers suitable for incorporation into the resin compositions of the invention we may mention styrene, chlorostyrene, vinyl toluene, diallyl phthalate and methyl methacrylate.

The ratio of the number of moles of the hydroxy component to the number of moles of the acid component is chosen so as to permit the desired molecular weight and acid number to be achieved. Thus when the polyester is made from reactants consisting of a dicarboxylic acid or acids and a mixture of glycols, the acid/glycol ratio is preferably chosen to be about 1:1 with the glycol in slight excess.

A preferred polyester is made by reacting with 2 moles of fumaric acid, 1.01 mole TCD-Alcohol DM and 1.01 mole of the reaction product of 1 mole Bisphenol A and 4 moles of propylene oxide.

The polyesters of the invention may be blended with other conventional polyesters and with a monomer to form resin compositions for a particular purpose.

The resin composition of the invention may include one or more conventional inhibitors, such as hydroquinone, 4-t-butyl catechol, benzoquinone or copper salts preferably in the range of 0.001% to 0.1% by weight based upon the polyester component of the mixture.

When the resin composition is to be used to prepare a casting or a laminate or other product, a polymerisation catalyst is usually used, for example a free radical catalyst such as benzoyl peroxide, t-butyl perbenzoate, cumene hydroperoxide or azobis (isobutyronitrile). Such catalysts are generally employed in amounts of 0.1 to 5% by weight based on the weight of the mixture of monomer and polyester, depending on the proportions of inhibitor and accelerator present in the mixture.

An accelerator may also be added to the resin composition to permit curing to commence without the application of external heat. Such accelerators include cobalt salts such as cobalt octoate or cobalt naphthenate in combination with methyl ethyl ketone peroxide and tertiary amines such as N,N-diethyl aniline in combination with benzoyl peroxide.

The resin composition may also incorporate conventional reinforcing fibres, such as glass fibres, fillers, such as calcium carbonate, and/or pigments.

In the following Examples, Example 1 is a comparative example illustrating that a resin based on glycols of formula (II) and without a glycol of formula (III) is brittle whereas Example 2 illustrates a resin in accordance with the invention and having a elongation at break above 2%, a heat deflection temperature above 100°C and good chemical resistance.

EXAMPLE 1

1.01 mole of TCD-Alcohol DM (trade name—Farbwerke Hoechst) and 1 mole fumaric acid were reacted at 195°C with stirring under a blanket of nitrogen until an acid value of 20 mg KOH/g was obtained. The resin was cooled to 140°C, 80 ppm hydroquinone added as inhibitor and blended with styrene monomer.

This resin had the following properties:

Viscosity at 25°C	=4.0 stokes
Volatile Content	=39%
Acid Value	=12.4 mg KOH/g
Gelation Time at 25°C using 2% Benzoyl Peroxide paste 0.2% Diethylaniline	=28.5 mins.

Cast sheets were made cured with 2% methyl ethyl ketone peroxide and 1% cobalt octoate. These were post-cured for 24 hours at room temperature and 3 hours at 80°C when the following properties were obtained.

Heat Deflection Temperature	145°C
Flexural Strength	7,100 lbf/in ²
Tensile Strength	2,400 lbf/in ²
Elongation at Break	0.7%
Tensile Modulus	0.39×10^5 lbf/in ²

After one year's immersion in boiling water and in 5% caustic soda at 80°C, no deterioration was apparent although the resin was very brittle.

EXAMPLE 2

1.01 mole TCD-Alcohol DM, 1.01 mole of the adduct made from 1 mole of Bisphenol A and 4 moles of propylene oxide and 2 moles fumaric acid were reacted at 195°C with stirring under a blanket of nitrogen until an acid value of 22 mg KOH/g was obtained. The resin was cooled to 140°C, 80 ppm of hydroquinone added as inhibitor and blended with styrene monomer.

The resin had the following properties:—

Viscosity at 25°C	=3.3 stokes
Volatile Content	=47%
Acid Value	=11.75 mg KOH/g
Gelation Time at 25°C using 2% Methyl Ethyl Ketone Peroxide and 0.5% Cobalt Octoate (12% Co)	=39 mins.

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When cast into sheets using 2% methyl ethyl ketone peroxide and 0.5% cobalt octoate as the curing system and post-cured for 24 hours at room temperature and 3 hours at 80°C the following properties were measured.

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Heat Deflection Temperature	114°C
Tensile Strength	7,800 lbf/in ²
Elongation at Break	2.8%
Tensile Modulus	0.485×10^5 lbf/in ²

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After 6 months' immersion in boiling water no deterioration was apparent. As a comparison a similar resin was made from 2 moles of fumaric acid, 1.01 mole TCD-Alcohol DMI and 1.01 mole of the adduct made from 1 mole of Bisphenol A and 2 moles of propylene oxide.

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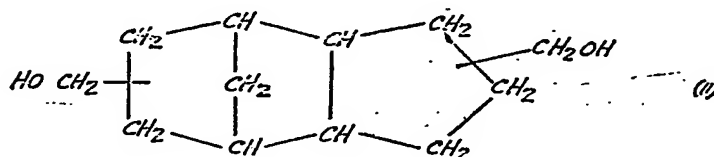
On curing, although this resisted 6 months' immersion in boiling water, it had become very brittle.

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WHAT WE CLAIM IS:—

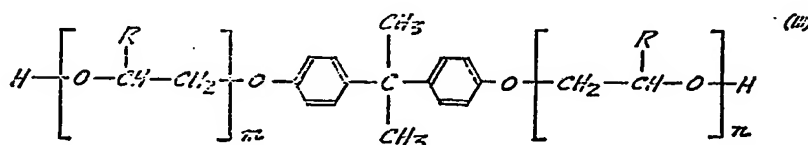
1. An unsaturated polyester which comprises the residues of (a) a glycol of the formula

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and (b) a glycol of the formula



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where R represents a hydrogen atom or a methyl group, and m and n are numbers and each has an average value of at least 1.5; and (c) at least one ethylenically unsaturated dicarboxylic acid.

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2. A polyester according to Claim 1, in which m and n each have an average value of 2 or more.

3. A polyester according to Claim 2, in which m and n each have an average value of 2 to 6.

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4. A polyester according to any one of claims 1 to 3, in which said glycol of formula (III) comprises the reaction product of 4 moles of ethylene oxide or propylene oxide with 1 mole of Bisphenol A.

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5. A polyester according to any one of Claims 1 to 4, in which a mixture of glycols of formula (II) is used.

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6. A polyester according to any one of Claims 1 to 5, in which the molar ratio of the glycol or glycols of formula (II) to the glycol or glycols of formula (III) is between 1:2 and 2:1.

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7. A polyester according to Claim 6, in which said molar ratio is about 1:1.

8. A polyester according to any one of Claims 1 to 7, in which said unsaturated carboxylic acid comprises maleic acid and/or anhydride and/or fumaric acid.
- 5 9. A polyester according to any one of claims 1 to 8, comprising the residues of 1.01 moles of a mixture of alcohols of formula (II), 1.01 moles of the reaction product of 1 mole of Bisphenol A with 4 moles of propylene oxide and 2 moles of fumaric acid. 5
10. A polyester according to Claim 1 substantially as herein described and exemplified.
- 10 11. A resin composition comprising an unsaturated polyester according to any one of Claim 1 to 10 and a copolymerisable monomeric ethylenically unsaturated compound. 10
- 15 12. A resin composition according to Claim 11, in which said copolymerisable compound comprises styrene, chlorostyrene, vinyl toluene, diallyl phthalate or methyl methacrylate.
- 15 13. A resin composition according to Claim 11 substantially as herein described and exemplified. 15

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